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HYDROGEN CYANIDE

(CAS 74-90-8 ; HCN)

SCOPE OF THE DOCUMENT

This document focuses on the hazards of hydrogen cyanide. The toxicity, fire and explosion hazards and reactivity of hydrogen cyanide are described. Details of protective measures, storage, handling, clean-up, disposal and first aid are also given. Information relevant to the workplace is emphasized. Special attention is given to the main hazards presented by hydrogen cyanide.

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HYDROGEN CYANIDE--CHEMICAL HAZARD SUMMARY NO. 39

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I. MAIN HAZARDS

Short-term exposure to hydrogen cyanide can be rapidly fatal. Hydrogen cyanide is unstable and can polymerize with explosive violence.

II. OCCUPATIONAL EXPOSURE

Hydrogen cyanide (HCN) is a colourless liquid at temperatures below 26.5°C (79.7°F). At normal room temperatures, HCN vapour concentrations can be quite high above the liquid. The vapour smells like bitter almonds and is normally detected at low concentrations (less than 5 ppm). However, since some people may not be able to smell HCN, the odour cannot be relied on as a warning sign of exposure.

HCN is commonly used in the production of the following chemicals:

- resin monomers, such as acrylates and methacrylates;
- cyanide salts, such as sodium cyanide; and
- nitriles, such as acrylonitrile.

HCN can be generated as a by-product during the operation of blast furnaces, gas works and coke ovens and during industrial processes, such as:

- electroplating,
- petroleum refining, and
- metallurgical and photographic processing.

HCN is sometimes used as a fumigant to exterminate rodents and insects. The burning of nitrogen-containing plastics, for example, polyurethanes, and some natural materials, for example, wool, can result in the release of HCN. Therefore, firefighters may be exposed to HCN vapours formed during a fire.

Breathing of HCN vapour is the most common route of exposure in the workplace. If direct contact occurs, liquid HCN rapidly enters the body through unbroken skin or the eyes. One report suggests that the vapour may be absorbed through unbroken skin if the airborne concentration is high [200 parts per million (ppm)].[1] Swallowing of liquid HCN is not common in the workplace but may occur if traces are present on hands, food, cigarettes or clothing.

General information on routes of exposure is available in the CCOHS publication "How Workplace Chemicals Enter the Body."[2]

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III. HEALTH HAZARDS

Removal from the Body

When HCN is absorbed into the body, most of it is broken down to a less toxic chemical called thiocyanate. This chemical is then excreted in the urine. A small amount of absorbed cyanide is excreted, unchanged, in the breath, saliva, sweat and urine.[3,4]

Effects of Short-Term Exposure in Humans

Inhalation

Not all exposures to HCN are fatal since the effect depends on both the concentration of HCN and the length of the exposure. Breathing 20 to 40 parts per million (ppm) of HCN for several hours may result in slight symptoms. At this level of exposure, the average person is able to break down HCN to the less harmful thiocyanate.[3,5,6]

HCN can be rapidly fatal once it overcomes the body's ability to cope. At concentrations slightly above 40 ppm, symptoms include weakness, giddiness, dizziness, headache, confusion, a drop in blood pressure, and, occasionally, nausea and vomiting. Breathing is rapid and deep at first, then becomes slow and gasping. The skin appears bright pink or red. The victim may feel an irregular heart beat and tightness in the chest. Uncontrollable urination and bowel movements may occur. Unconsciousness, convulsions and death quickly follow. Massive doses produce, without warning, sudden unconsciousness and immediate death. An airborne concentration of 270 ppm can be fatal in one minute.

If poisoning does not result in death, recovery is usually complete. However, there have been a few reports of after-effects. Since HCN stops cells from using oxygen, it is possible that some permanent damage to the central nervous system may result. These effects are rare and are similar to the effects seen in people who have been deprived of oxygen for other reasons (for example, near-drowning victims).[5]

Eyes

Liquid HCN is slightly irritating to the eyes upon direct contact. Since the liquid is rapidly absorbed through the eyes, symptoms similar to those caused by inhalation may be experienced if a sufficiently large amount is absorbed.

HCN vapour may cause visual disturbances by damaging the retina and the nerve of the eye. In most cases, poisonings that have resulted in impaired or lost vision have been caused by a very high exposure.[11]

Skin

Liquid HCN does not irritate the skin. It can, however, be rapidly absorbed into the body through unbroken skin. The symptoms which result are the same as those caused by inhalation of HCN. There have been reports of deaths caused by HCN which has been absorbed through the skin.

There is one report of concentrated HCN vapour being absorbed through unbroken skin.[1] The vapour concentration was about 200 ppm and the exposed people were wearing the correct respiratory protection. They experienced symptoms of HCN poisoning after a short exposure.

Ingestion

Ingestion of HCN is rare in the workplace.

If ingested, liquid HCN is very rapidly absorbed through the stomach lining. Symptoms are the same as those described for inhalation. In addition, there may be a bitter, pungent or acrid, burning taste in the mouth. Sometimes there is a feeling of numbness or tightness in the throat and stiffness in the lower jaw. Salivation, nausea and vomiting often follow. An odour of bitter almonds may be on the breath or vomit.

Effects of Long-Term Exposure in Humans

Carcinogenic Effects

No increase in cancer has been reported for humans exposed to HCN or other cyanide compounds for a long time. There have been no animal studies done on the potential cancer-causing ability of HCN.

Effects on Body Tissues and Organs

A wide range of symptoms have reportedly been caused by long-term exposure to low levels (often less than 10 ppm) of HCN. These symptoms may include some or all of the following:

- persistent runny nose
- weakness
- dizziness
- giddiness
- headache
- nausea
- abdominal pain
- vomiting
- throat irritation
- changes in taste and smell
- muscle cramps
- weight loss
- flushing of the face
- enlargement of the thyroid gland

Some scientists believe that these effects are definitely related to long-term, low-level exposure to HCN.[4,6,7] Others do not rule out the possibility that long-term HCN poisoning occurs but suggest that more definite proof is necessary.[3]

It has been difficult to prove that chronic HCN poisoning exists for a number of reasons. First, the condition is rare. Very few cases have been described, and sometimes it is not clear that HCN exposure caused the symptoms. Second, many of the symptoms described are not unique to HCN. Any number of other chemicals, such as solvents, or illnesses, such as the flu, can cause the same kinds of symptoms.

It has been suggested that chronic HCN poisoning is rare because only certain people are susceptible. HCN is broken down by the body to thiocyanate. In most people, the thiocyanate is then excreted in the urine. However, for reasons

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which are not understood, some people may not be able to eliminate thiocyanate from the body as readily as others. They may then experience health effects caused by the thiocyanate.[8] This is possible, since the health effects believed to be caused by long-term exposure to HCN are similar to those described for thiocyanate poisoning.

Two fairly recent studies[9,10] have reported higher thiocyanate levels in people exposed to low levels of HCN over a long period of time. In both studies, the workers were described as having symptoms "typical" of chronic HCN poisoning. These studies strengthen the argument that long-term exposure to HCN increases thiocyanate in the body, which in turn causes adverse health effects.

The scientists who have reported chronic HCN poisoning seem to agree that the symptoms disappear once the affected person is removed from HCN exposure. However, the symptoms quickly reappear once the individual returns to work with HCN.

In rare cases, exposure to low levels of HCN irritates the eyes. There is also some concern that low-level, long-term exposure to HCN may damage the nerves of the eyes.[11]

One report mentions that long-term, low-level exposure to HCN may cause a temporary blotchy rash on the face.[4]

Reproductive Effects

There have been no reports of any adverse reproductive effects in people working with HCN. However, if HCN exposure is high enough to cause symptoms in the mother, effects would also be expected in the unborn child.

Toxicity Data in Animals and Laboratory Tests

Lethal Dose Values

The poisoning strength of a compound can be estimated from the LD_{50} or LC_{50} obtained in animal tests. LD stands for lethal dose; LC for lethal concentration in air. The LD_{50} is the amount of a chemical (weight of chemical per weight of animal) which is needed to kill one-half (50 percent) of the test animals. The LC_{50} is the concentration in air which kills one-half of the animals following an exposure lasting 4 hours or another indicated time period. Test animals are usually rats, mice or other rodents. Routes of exposure are usually by mouth (oral), through the skin (dermal) or by breathing in the airborne chemical (inhalation). The values obtained for this material by different researchers are:

LD_{50} (mouse, oral): 3.7 mg/kg[12]
LC_{50} (rat, inhalation): 142 ppm/30 minutes[13]
LC_{50} (rat, inhalation): 484 ppm/5 minutes[12]
LC_{50} (mouse, inhalation): 169 ppm/30 minutes[14]
LC_{50} (mouse, inhalation): 323 ppm/5 minutes[12]

Further general information on the LD_{50} is available in the Centre's publication "What is an LD_{50}?"[15]

IV. FIRE AND EXPLOSION HAZARDS

The fire or explosion hazard of a substance is normally described by the flash point and flammable or explosive limits.

The flash point of liquid HCN is -18°C (-0.4°F). When HCN approaches this temperature, enough vapour is produced near the surface of the liquid to form a flammable or explosive mixture of vapour and air. An ignition source will cause this mixture to burn or explode.

The flammable or explosive range of HCN in air is 5.6-40.0% (56 000-400 000 ppm). The HCN vapour concentration above the liquid can be very high, especially in a confined space. Therefore, concentrations within the flammable range may be encountered frequently. The lowest concentration of the material in air which can burn or explode is called the Lower Explosive Limit (LEL) or the Lower Flammable Limit (LFL). The LEL for HCN is about 5.6%. Similarly, the highest concentration of the material in air which can burn or explode is called the Upper Explosive Limit (UEL) or the Upper Flammable Limit (UFL). The UEL for HCN is 40.0%. Between the LEL and the UEL, hazards include the possibility of explosion in confined spaces or the possibility of flashback: a fire travelling along the line of vapour or gas from a spark or flame to a container or spill. When the concentration is below the LEL, the air/chemical mixture is too "lean" to burn, and when the concentration is over the UEL, the mixture is too "rich."

Adequate ventilation can prevent the accumulation of explosive concentrations of the airborne material in work or storage areas.

V. CHEMICAL REACTIVITY

Liquid HCN and HCN solutions in water are dangerously reactive and can polymerize with explosive violence. Polymerization is a chemical reaction which can generate a lot of heat. If heat builds up in the container of HCN, an explosion may occur.

HCN liquid or gas becomes less stable and may polymerize under certain conditions:

- if it has been stored more than 90 days,
- if it contains more than 2-5% water,
- if it is heated to temperatures equal to or above 184°C (365°F),
- if it has not been properly stabilized with a small amount of acid by the manufacturer, or
- if it comes into contact with a base (compounds with a pH greater than 7).

HCN can react with a wide range of other chemicals. These reactions are not usually vigorous unless the other chemical is highly reactive. Fluorine and ozone are examples of highly reactive chemicals.

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VI. EXPOSURE LIMITS

Many Canadian jurisdictions have workplace exposure limits for airborne chemicals similar to those established by the American Conference of Governmental Industrial Hygienists (ACGIH). The following exposure limit has been established by ACGIH for airborne HCN: a ceiling limit of 10 parts per million (ppm) or 10 milligrams per cubic metre (mg/m^3) (skin).*

*"Skin" Notation: Absorption by the unbroken skin, eyes or mucous membranes may contribute to the overall exposure.

Contact the appropriate authority in your jurisdiction for details of the specific regulations which apply. Refer to ACGIH documentation for information on the exposure limits.

VII. EXPOSURE CONTROLS

Exposure to HCN can be controlled in many ways. The control measures appropriate for a particular work site depend on how the HCN is used or generated as a by-product, and the extent of exposure. The general information given in this section should be used to develop specific control measures for your work site. You should ensure that control systems are properly designed and maintained and that you comply with occupational, environmental, fire and other applicable regulations.

Engineering Controls

Engineering control methods to reduce hazardous exposures are preferred over other measures. Engineering control methods include mechanical ventilation (dilution and local exhaust), process or personnel enclosure, control of process conditions, and process modification (for example, substitution of a less hazardous material).

Stringent control measures such as enclosure or isolation and local exhaust ventilation may be necessary because of the high potential hazard associated with HCN. A non-sparking, grounded ventilation system separate from other exhaust ventilation systems should be used. Ventilation systems should be exhausted through a scrubber to the outside. Sufficient replacement air should be supplied to make up for air removed by exhaust systems.

Personal Protective Equipment

If engineering controls and work practices are not effective in controlling exposure to HCN, then suitable personal protective equipment including approved respiratory protection, should be worn. In addition, appropriate equipment should be available for use in emergencies such as a spill or fire.

Chemical safety goggles should be worn to protect the eyes from HCN. A face shield may also be necessary to protect the face. Gloves, coveralls, boots and/or other protective clothing which is resistant to HCN should be worn to protect the skin. An impervious full-body encapsulating suit and respiratory protection may also be required in some operations. Materials which have a good

resistance to HCN include butyl rubber, neoprene, polyethylene and Viton.[16] The resistance of specific materials can vary from product to product. Resistance should be evaluated under the actual conditions of use. All protective equipment should be carefully maintained.

Respiratory Protection

If respiratory protection is required, a complete respiratory protection program including selection, fit testing, training, maintenance and inspection should be instituted. These factors are described in detail in the CSA Standard Z94.4 "Selection, Care and Use of Respirators," which is available from the Canadian Standards Association, Rexdale, Ontario, M5W 1R3.

The degree of respiratory protection required depends on the concentration of the vapour and the duration of exposure. The U.S. National Institute for Occupational Safety and Health (NIOSH)[17] recommends the following respiratory protection for HCN vapour concentrations:*

Up to 47 ppm: Any supplied-air respirator, or any self-contained breathing apparatus.

Up to 50 ppm: Any supplied air respirator operated in a continuous-flow mode, or any self-contained breathing apparatus with a full facepiece, or any supplied-air respirator with a full facepiece.

Emergency or planned entry in unknown concentration or IDLH conditions**: Any self-contained breathing apparatus with full facepiece and operated in a pressure-demand or other positive-pressure mode, or any supplied-air respirator with a full facepiece and operated in pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.

* These recommendations apply only to NIOSH and MSHA (Mine Safety and Health Administration) approved respirators.

** IDLH (Immediately Dangerous to Life or Health): For the purpose of respirator selection, IDLH concentration is defined as the maximum concentration from which one could escape within 30 minutes without any escape-impairing symptoms or irreversible health effects. The IDLH for HCN is 50 ppm.

VIII. SMALL-SCALE STORAGE AND HANDLING

HCN should be stored in a cool, dry, well-ventilated area, out of direct sunlight. It should also be stored away from heat and ignition sources, incompatible materials and water or products containing water. Containers of HCN should not be stored more than 90 days, or as recommended by the manufacturer.

HCN is very flammable. Therefore, grounded, non-sparking ventilation systems and electrical equipment that does not provide a source of ignition should be used in storage facilities, if needed. Suitable, approved storage cabinets,

tanks, rooms and buildings should be used. If small quantities of HCN are stored under refrigeration, an approved, explosion-proof refrigerator should be used. Comply with all applicable regulations for storage and handling of flammable materials.

The quantity of HCN in storage should be limited. As well, the use of leak detection and alarm systems should be considered. Access to storage areas should be restricted and the storage area kept separate from work areas. Containers should be inspected periodically for damage or leaks.

Cylinders of hydrogen cyanide must be stored in a vertical position and be adequately grounded and supported. Cylinders should not be dropped or damaged, and no part of the cylinder should be heated to a temperature higher than 50°C. Full cylinders should be stored separately from empty ones, and all empty cylinders should be labelled.

No one should work alone with HCN. Another person must be in view at all times and must be equipped and trained to execute a rescue. If HCN is accidentally released into the work environment, everyone in the area must immediately put on a respirator and leave the area until the severity of the release is determined. Emergency equipment should always be readily available.

The smallest amount of HCN possible should be used, and only in designated areas with adequate ventilation. HCN must be kept away from ignition sources. "NO SMOKING" signs should be posted in areas where HCN is used. HCN should not be used near welding operations, flames and hot surfaces. It also should be kept away from water and other incompatible materials.

Containers of HCN should be labelled and kept closed when not in use. Empty containers may contain residues which are hazardous. Do not attempt to open a container if it is of unknown age.

Cylinders of HCN should be moved by a hand-truck or a cart designed for this purpose. Cylinders should not be lifted by their caps, dropped or permitted to bang against other cylinders. The valve cap should be left on the cylinder until it is secured and ready for use. All valves should be closed and checked before and after withdrawing HCN from the cylinder. Do not trap HCN between two valves.

IX. FIRST AID

The following general procedures are suggested for first aid when an exposure to HCN occurs.

Inhalation

Before attempting to rescue the HCN victim, take proper precautions to ensure your own safety; for example, wear appropriate protective equipment and use the "buddy" system. Then, remove the source of HCN contamination or move the victim to fresh air. Refer to the General Comments section below for additional first aid and antidote information.

Eye Contact

Immediately flush the contaminated eye(s) with gently flowing water for at least 20 minutes while holding the eyelid(s) open. Take care not to rinse the contaminated water into the non-affected eye. Refer to the General Comments section below for additional first aid and antidote information.

Skin Contact

The rescuer should avoid any direct contact with HCN by wearing protective gloves which are resistant to this chemical, if necessary. As quickly as possible, flush the contaminated skin with lukewarm, gently running water for at least 20 minutes. Under running water, remove contaminated clothing, shoes and leather goods (for example, watchbands or belts). Contaminated clothing, shoes, and leather goods should be discarded. Refer to the General Comments section below for additional first aid and antidote information.

Ingestion

Never give anything by mouth if the victim is rapidly losing consciousness, or is unconscious or convulsing. Do not induce vomiting. Instead, have the victim drink 240 to 300 mL (8 to 10 oz.) of water. If vomiting occurs naturally, have the victim rinse his or her mouth and repeat the administration of water. Refer to the General Comments section below for additional first aid and antidote information.

General Comments

If the victim has difficulty breathing, is becoming confused or is losing consciousness, amyl nitrite should be administered by a person trained in its use. One pearl of amyl nitrite should be crushed onto a cloth and held to the victim's nose 15 to 30 seconds of each minute. A new pearl should be used every 5 minutes (0.3 mg size) or every 3 minutes (0.18 mg size). While the amyl nitrite is being used, the victim's blood pressure should be monitored by a trained person. If the blood pressure drops below 80/60, the amyl nitrite should be stopped and the opinion of a physician obtained immediately.

Oxygen should be administered by a person trained in its use. If breathing has stopped, a trained person should begin artificial respiration, or if the heart has stopped, cardiopulmonary resuscitation (CPR), immediately. Avoid mouth-to-mouth contact.

The victim should be transported quickly to an emergency facility. General supportive measures such as comfort, warmth and rest should be provided.

A physician and/or the nearest Poison Control Centre should be consulted for all exposures in which the victim experiences symptoms related to HCN exposure.

Some recommendations in this section may be considered medical acts in some jurisdictions. These recommendations should be reviewed with a physician, and appropriate delegation of authority should be obtained, as required. All of the first aid procedures should be periodically reviewed by a physician familiar with the health hazards of HCN and its conditions of use in the workplace.

X. FIREFIGHTING

HCN vapour is extremely toxic. Therefore, the area around a fire where HCN vapours may be formed must be evacuated. Fires should be fought from a safe distance or a protected location. Firefighters should stay upwind and avoid contact with HCN.

HCN vapours are extremely flammable. The vapours may travel to a source of ignition and flash back or may explode if ignited in an enclosed area.

Containers of HCN may explode in the heat of a fire. If it is possible to do so without risk, containers should be removed from the fire area. Emergency personnel should stay away from the ends of containers or tanks and should withdraw immediately if there is a rising sound from the safety venting device or any discolouration of the container or tank.

Any leak or discharge of HCN should be stopped immediately, if it is possible to do so safely. In the case of a small fire, if it is not possible to stop the leak, the fire should be allowed to burn itself out if there is no risk to the surroundings.

Small fires involving HCN can be extinguished with dry chemical, carbon dioxide, water spray or foam. For large fires, water spray, fog or foam should be used. Water may be ineffective as an extinguisher but can be used to keep fire-exposed containers cool, to disperse HCN vapours, to flush spills of hydrogen cyanide away from areas occupied by people, to dilute spills to make non-flammable mixtures, or to protect rescue workers trying to stop a leak or discharge.

XI. CLEAN-UP AND DISPOSAL

An emergency action plan should be prepared in advance and appropriate training provided for emergency response personnel. Emergency equipment should be readily available and in good working order.

In case of an emergency, access to the area should be restricted until completion of the clean-up. The clean-up should be conducted by trained personnel only. Adequate protective equipment should be worn and the contaminated area ventilated. All ignition sources should be extinguished or removed from the area. Flammable and combustible materials should also be removed or isolated.

Government occupational and environmental authorities should be notified that a spill has occurred.

Emergency personnel should not touch the spilled HCN, and should prevent it from entering sewers or confined spaces. The leak should be stopped or reduced if it can be done safely. If the source of leak is a cylinder and the leak cannot be stopped, the leaking cylinder should be removed to a safe place in the open air. Then, the leak can be repaired or the cylinder allowed to completely empty. The spill can be contained with earth, sand or other absorbent material which will not react with the spilled HCN.

For small spills of liquid HCN, the spill should be soaked up with an absorbent material and put into a suitable, covered, labelled container. The area should then be flushed with water, taking care that the water does not get inside the containers or directly on the spilled HCN. The contaminated absorbent material may pose the same hazard as the spilled HCN.

For a large spill, fire and emergency services and the supplier should be contacted for advice.

Federal, provincial and local government requirements should be reviewed before the removal of waste HCN. Material for disposal should be stored as described in Storage and Handling. Disposal by controlled incineration or secure landfill may be acceptable.

Waste solutions of HCN can be decontaminated by making the solution strongly basic (pH 12) with caustic and pouring it in a ferrous sulfate solution. The resulting ferrocyanide is relatively harmless.

Waste solutions of HCN can also be converted to the less toxic cyanate by treatment with chlorine, sodium hypochlorite, calcium hypochlorite or ozone at pH 9-11. A maximum amount of 10% hypochlorite should be used. The final solution should be checked for the absence of free cyanide.

Decontamination of waste cyanide solutions must be done by specially trained personnel. Disposal of treated solutions by secure landfill may be acceptable.

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Note: Additional references on this subject are available from CCOHS upon request.

PLEASE NOTE

This summary was prepared at the Canadian Centre for Occupational Health and Safety (CCOHS) and is intended primarily as a source of information for persons who work with or may be occupationally exposed to this material. The information selected for inclusion is believed to be reliable and generally relevant to occupational health. Other information which bears on particular work situations may be available. The scientific data in many areas are limited and may allow a variety of interpretations. Additional information, corrections, comments and questions are welcome, and should be addressed to the Inquiries Service, CCOHS, 250 Main Street East, Hamilton, Ontario, L8N 1H6, (416) 572-2981; toll free 1-800-263-8276.

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